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(54) PROCESS FOR THE TREATMENT OF WASTE WATER

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(71) We, STAMICARBON B.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to a process for the treatment of waste water.

Carbonaceous and nitrogeneous impurities may be removed from water wastes by biological treatment. However, complete removal of carbonaceous impurities generally cannot be attained due to the presence in the waste water of biologically non-degradable components.

Biologically non-degradable carbonaceous impurities may however be removed by the so-called Zimmermann process (see for example U.S. patent specification 2,665,249). In this process organic compounds are oxidized in the aqueous phase under elevated temperature and pressure by means of molecular oxygen to yield gaseous reaction products mainly carbon monoxide, carbon dioxide and water. This type of process suffers however from a major disadvantage in that high working pressure is required, entailing the use of costly high-pressure equipment and the necessity to compress large quantities of oxygen e.g. air. Compression costs are an important item in ascertaining the economic viability of a process. While some of the energy used in compression may be recovered from the reactor off gases, the recovery efficiency is satisfactory only for very large installations. Thus such processes for purifying waste water on a medium or small industrial scale are costly and therefore unsuitable.

It has now been found that this disadvantage may be overcome if the molecular oxygen, the oxidizing agent, is replaced in whole or in part by nitric acid and/or a nitrate. It is possible then to operate at a lower pressure, and use a reactor of considerably smaller dimensions, thereby reducing the plant investment cost. The expensive oxygen-compression

stage can be omitted, and replaced by a much cheaper liquid compression stage. Furthermore the cost of the oxidation agents used according to the invention may be suppressed by using very cheap waste nitrate and/or waste nitric acid.

Thus the invention provides a process for the treatment of a waste water whereby carbonaceous contaminants contained in the waste water are converted to gaseous reaction products comprising oxidizing the said contaminants in the waste water with an oxidation agent which is nitric acid and/or a nitrate at a temperature between 150°C and the critical temperature of the water containing the contaminants.

In the process according to the invention the operating pressure needs only to be sufficiently high to maintain a liquid phase at the prevailing temperature. The minimum working pressure thus equals the vapour pressure of the liquid at the prevailing temperature. In practice, the working pressure is slightly higher than the minimum pressure, for example from 0.5 to 10, preferably from 0.5 to 5 atmospheres above the said minimum pressure. Higher pressures, e.g. in excess of 500 atmospheres are undesirable for the reasons hereinbefore set forth.

At a temperature exceeding the upper limit it is not possible to maintain a liquid phase. At temperatures below the lower limit, the reaction rate is insufficient, and substantially complete conversion of the organic impurities into gaseous reaction products mainly carbon dioxide and water vapour, is not achieved. At a temperature between 150 and 220°C, the reaction usually proceeds at a sufficiently fast rate, although certain types of waste water yield not only gaseous reaction products but also other undesired products. Above 220°C, organic products can be converted at least 95% into gaseous products, and such higher temperatures are to be preferred.

Thus a particularly preferred temperature is between 250 and 310°C, whereby removal of the impurities may readily be achieved within a reasonable time with reasonable

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	pressure requirements for maintaining a liquid phase. At 250°C the minimum working pressure is 39 atmospheres and at 310°C it is 97 atmospheres. In known process where air is	reaction products. Although dinitrogen monoxide is more easy to handle than other nitrogen oxides, and its reduction to nitrogen can be effected in a simple manner, nevertheless nitrogen is the preferred reaction product for environmental reasons. A further advantage of the use of ammonium nitrate compared with nitric acid lies in the higher pH and hence, in the lower corrosiveness, of the reaction mixture.	70
5	used as the oxidation agent, a working pressure higher by 30 to 55 atmospheres is necessary in this temperature range. The rate of reaction increases with the temperature and decreases with increasing pH of the reaction		
10	mixture.		75
	A particular feature of the reaction conditions of the process according to the invention is that at least at temperatures above 220°C, the nitric acid and/or the nitrate reduced in	Furthermore ammonium nitrate may be present in large excess without giving rise to nitrous fumes, unconverted ammonium nitrate remaining in the treated water.	
15	the process, is substantially completely converted to molecular nitrogen and a small amount of dinitrogenmonoxide. Substantially no nitrous fumes (nitrogen monoxide and nitrogen dioxide) are produced, even if nitric	The ammonium nitrate oxidant used in the process according to the invention may comprise a mixture containing nitrate ions and ammonium ions in a ratio differing from 1. Such an oxidant may be regarded as a mixture containing ammonium nitrate, and it behaves as such.	80
20	acid is used as the oxidation agent, provided the nitric acid is not present in a substantial excess e.g. 50% based on the carbonaceous substances to be oxidized. By comparison the oxidation of organic substances		85
25	with nitric acid under reaction conditions outside that of the invention may result in the formation of nitrous fumes. The absence of nitrous fumes in the process according to the invention renders it particularly suitable	Oxidizing agents in addition to nitrate and/or nitric acid, may be used, for example, the nitrate and/or nitric acid may be partly replaced by oxygen. This may be necessary in those instances where the available nitrate and/or nitric acid is present in too low a concentration for oxidizing the material to the required degree. However under such conditions the advantages resulting from the use of lower working pressure and lower compression expenses will then become partly lost.	90
30	for technical applications, as the blowoff of nitrous fumes is environmentally undesirable and the absorption of nitrous fumes from a gas with a low concentration of nitrogen oxides is difficult to achieve. An equivalent of nitric		95
35	acid for use in the process according to the invention is provided by a mixture of a nitrate and a strong acid.	Water wastes containing carbonaceous substances may be derived from many sources, for example cellulose-containing effluent from paper mills, and water wastes from chemical plants or sewage sludge suspensions. The impurities to be oxidized in the water wastes may be present therein in dissolved or in solid form, for example as a suspension.	100
40	If nitric acid is used as the oxidation agent, it is preferably used in an amount less than 50% excess based on the carbonaceous substances in the waste water, whereby no nitrous fumes are produced and the carbonaceous products are broken down to a high degree. To achieve a sufficient degree of conversion	The process according to the invention is also suitable for treating waste streams which contain salts in addition to carbonaceous waste material. With such streams the treatment leaves a purified salt solution from which pure crystalline salt can be recovered in a simple manner. Processing such waste by previously known processes involves substantial technical difficulties and expense. Waste water contaminated with organic substances and containing salts is an environmental hazard, particularly if drainage is into inland waters. The process according to the invention enables such waste streams to be processed in a simple manner.	105
45	within a reasonable time, an excess of from 10% to 25% of nitric acid is generally sufficient.		110
	A particularly suitable oxidant for use in the process according to the invention is ammonium nitrate. A further advantage of the use of ammonium nitrate is that it disappears completely under the reaction conditions, the ammonium ion being oxidized to nitrogen and water and the nitrate ion being		115
50	reduced to molecular nitrogen, some dinitrogen monoxide (laughing gas) being also formed. Thus by the use of ammonium nitrate, only gaseous reaction products are formed. Other inorganic nitrates leave their cation in the waste water.		120
55		The process according to the invention can be carried out either batchwise or continuously. Since the oxidation reaction is exothermic, useful energy can be recovered under suitable conditions, for example from reactor off-gases. In a continuous process, heat can be exchanged between the issuing purified water and the inflowing reaction mixture or its components.	125
60	Compared with nitric acid oxidant (which also results in the formation only of gaseous reaction products) ammonium nitrate has the advantage that less dinitrogen monoxide and more molecular nitrogen are produced as	By appropriate selection of the operating	130
65			

conditions, it is possible for resulting heat balance to enable the process to be self-supporting.

A catalyst, for example a salt of a transition metal may be incorporated in the reaction mixture. Since it is undesirable to discharge such a salt into surface waters, it should in most instances be subsequently eliminated from the reaction mixture, after the reaction has been completed. The oxidation reaction however proceeds satisfactorily if no catalyst is present.

The process according to the invention is particularly suitable for treating waste water which contains nitrogen compounds in addition to carbonaceous impurities. Both inorganically bonded nitrogen e.g. nitrate, nitrite and ammonia, and organically bonded nitrogen may be removed by the process of the invention by conversion into molecular nitrogen, and thus the process according to the invention offers a great advantage over the hitherto-used Zimmermann process in which organically bonded nitrogen is converted substantially to ammonia, which results in inconvenience and, due to the high degree of dilution, is difficult to remove in an economically acceptable manner. This problem does not occur in the process according to the invention.

An example of waste water which contains a large proportion of nitrogen in the form of ammonia in addition to carbonaceous impurities which can effectively be purified by the process according to the invention, but not by processes hitherto used is the effluent waste water of an industrial chemical complex where organo chemical conversions are carried out as well as operations involving the use of ammonia, nitric acid, urea and/or melamine. A particular example of such a plant is a caprolactam plant which uses a production process following the route:

Atmospheric nitrogen → ammonia → nitric acid → hydroxylamine → cyclohexanone oxime → caprolactam.

The process according to the invention can be used with particular advantage for treating aqueous effluents comprising ammonia salts contaminated with organic substances. In many processes, an inorganic acid usually sulfuric acid, or possibly phosphoric acid is used and converted into an ammonium salt contaminated with carbonaceous substances. An example is the preparation of acrylonitrile from propylene, ammonia and a gas containing molecular oxygen. In such an acid treated mixture unconverted ammonia is bonded as ammonium sulfate. Upon evaporation of the aqueous solution to remove acrylonitrile, there remains an ammonium sulfate solution that is highly contaminated with organic substances. Other examples are the corresponding preparation of methacrylonitrile from isobutylene, ammonia and a gas containing molecular oxygen; the preparation of methyl-

methacrylate from acetone cyanohydrin, methanol and sulphuric acid; the preparation of a lactam from a cycloaliphatic oxime, e.g. of caprolactam from cyclohexanone oxime, by rearrangement with sulphuric acid followed by neutralization with ammonia; and the refining of crude mineral oil to provide a tar containing ammonium sulphonates.

The processing of such ammonium salt solutions contaminated with organic materials to pure crystalline ammonium salt and an organic mixture that can be used as a fuel, is a costly operation. In many instances, the purified crystalline ammonium salt is of inferior quality, while the organic mixture is often corrosive and it not suitable for use as a fuel oil in conventional furnaces. Furthermore even highly refined ammonium sulphate is difficult to sell at an economic price.

The discharge of aqueous ammonium salt solutions contaminated with organic substances is undesirable due to environmental factors and in many instances is in fact prohibited by the authorities or, heavily penalised.

The process according to the invention when applied to effluents and product solutions as hereinbefore described provides for the recirculation of an inorganic acid which during use as an auxiliary material in a given process, becomes converted to a contaminated ammonium salt. The excessive production of ammonium sulphate by-product, is thus avoided. Such features are also of importance when considered in relationship to the need of curbing the depletion of natural resources, e.g. that of sulphur which is necessary for the production of sulfuric acid.

During the oxidation with nitric acid of waste water containing carbonaceous impurities and an ammonium salt, both the carbonaceous impurities and ammonium ions are converted to gaseous oxidation products. The conversion of the latter is effected readily due to the surprising fact that the oxidation of ammonia ions to molecular nitrogen by means of nitric acid proceeds much faster in the presence of carbonaceous impurities than in the absence thereof. This has the result that after the oxidation reaction there remains a purified solution of inorganic acid, which after concentration, or dilution, may be re-used in e.g. recycled to the process.

Ammonium salts which may thus be processed may be derived from an inorganic acid, or from an acid which under the reaction conditions becomes converted to an inorganic acid. Examples of such salts are sulfates, phosphates, sulfites, arsenates, selenates and organic sulfonates, sulfinates and phosphonates. Under the reaction conditions the last three undergo oxidation of the organic part of the molecule, and are converted to sulfuric acid, and phosphoric acid, respectively.

The process according to the invention is particularly suitable for the processing of waste

water obtained in the preparation of an unsaturated nitrile from gas containing an alkene, ammonia and molecular oxygen, for example in the preparation of (meth)acrylonitrile hereinbefore described. Such waste water contains considerable quantities of biologically undegradable components. Owing to the nature and the volume of the organic impurities, purification of such waste water by means of the known technique is a very difficult and costly operation. A conventional approach to the problem includes an extractive crystallisation step of the ammonium sulfate contained in the waste water. This technique yields good results, but is expensive. The process according to the invention does not require the use of an expensive extraction agent, and no crystalline ammonium sulfate or an organic residue that is difficult to process has to be disposed of.

The following examples of the invention are provided.

EXAMPLES I—III

125 ml of water were introduced to a 5-litre chromium-nickel steel autoclave provided with a stirrer. The autoclave was closed and heated to 300°C 300 ml of waste water from a caprolactam plant, to which ammonium nitrate has been added, were then introduced into the autoclave with nitrogen. The organic impurities in the waste water consisted mainly of caprolactam, aminocaproic acid and related compounds, and it also contained 0.67 g of ammonium sulphate per g of COD. The chemical oxygen demand (COD) of the reaction mixture, as determined by the dichromate method, initially was 84.0 g/litre, and its nitrate oxygen content was 176 g/litre. The pH was adjusted to 8.0. The temperature was then raised to 247°C and maintained at that value. The pressure in the autoclave was not higher than 38 atmospheres gauge.

After the reaction had been maintained for 30 minutes, with stirring, the COD fell to 50% of the initial value, after 60 minutes to 43% and after 120 minutes to 37%, the final pH being 3.0.

When the autoclave was opened it was found that gaseous reaction products had formed, consisting mainly of carbon oxides and molecular nitrogen, some dinitrogen monoxide also being present. The off gas was colourless, and did not assume a reddish-brown coloration upon exposure to air, indicating that nitrous fumes were substantially absent.

When the process was carried out at 280°C, under similar conditions, the COD after 30 minutes did not exceed 29% of the initial value, and not nitrous fumes were observed. If more ammonium nitrate is added to the waste water, so that at the start of the reaction the mixture contained 300 g of nitrate nitrogen per litre, and the temperature used was 300°C,

the COD decreased to 20% of the initial value in 30 minutes and to 3% in 150 minutes. Nitrous fumes were not observed.

In an experiment conducted in conformity with the latter procedure, analyses of the gas in the autoclave before and after the reaction yielded the following figures:

	Before the reaction; %-volume	After the reaction; %-volume	
N ₂	99.5	91.5	
O ₂	0.4	<10 ⁻⁴	75
N ₂ O	<10 ⁻⁴	0.5	
H ₂	<10 ⁻⁴	0.7	
CO ₂	10 ⁻³	4.6	
CO	<10 ⁻⁴	0.4	
H ₂ O	<10 ⁻⁴	2.3	80
NO+NO ₂	<0.1	<10 ⁻²	

EXAMPLE IV

The procedure of Examples I to III was repeated using waste water from a caprolactam plant that had been concentrated by evaporation, and admixed with sufficient ammonium nitrate, so that at the start of the reaction the mixture had a COD content of 158.0 g/litre and a nitrate oxygen content of 1200 g/litre. The working temperature was 255°C and the initial pressure 60 atmospheres gauge. The said pressure being obtained by forcing air into the autoclave until the oxygen partial pressure at 255°C equals 4 atmospheres. The pH at the start of the reaction was 2.2.

After 5 minutes reaction time, the COD had decreased to 40% of the initial value, after 30 minutes to 26%, and after 90 minutes to 9%. No nitrous fumes are observed in the gaseous reaction products.

EXAMPLE V

Using a similar procedure to Examples I—III a reaction mixture was used with COD content of 78.0 g/l and a nitrate oxygen content of 155 g/litre. The nitrate oxygen did not originate from ammonium nitrate, but from nitric acid. The initial pH was 0.3. The reaction temperature was 300°C.

After 15 minutes, the COD had fallen to 6% of the initial value and after 90 minutes to 3%. No nitrous fumes were observed.

EXAMPLE VI

100 g of ammonium nitrate were added to 1 litre of a thickened suspension of activated sludge with a COD of 20.7 g/litre and the mixture heated to 300°C and maintained at that value in a closed stirred autoclave. The initial pH was 6.6 After 5 minutes reaction the COD was fallen to 33% of the initial value. After 30 minutes this number was 25% and 4.5 g/litre of solid matter had formed. After 120 minutes reaction, the COD was 20% of the initial value and 4.6 g/litre of solid matter had formed, which contributed

initial a -150 ved. ormity he gas action	65 70	1.2 g/litre to the COD content of the suspension, the pH being 7.4. Nitrous fumes were not observed.	EXAMPLE X Waste water from the preparation of acrylonitrile from propene was mixed with nitric acid to form a reaction mixture containing 27.5 g/litre of organic impurities (as COD), 27.4 g/litres of nitrate (as nitrogen) and 37.4 g/litre of Kjeldahl nitrogen.	65
action; me 5 0-4 5 7 6 4 3 0-2	75 80	EXAMPLE VII 5 A synthetic waste water contaminated with caprolactam, the sodium salt of aminocaproic acid, and sodium sulfate, was stirred with nitric acid in a 5-litre autoclave to form 900 ml of a reaction mixture containing 28.8 g/litre of caprolactam, 28.8 g/litre of the sodium salt of aminocaproic acid, 86.4 g/litre of sodium sulfate and 157 g/litre of nitric acid, the mixture having a pH of 0.4. The amount of nitric acid present was 19% in excess based on the COD content of the liquid.	1900 Milliliters of this reaction mixture were placed in a 5-litre chromium-nickel steel autoclave provided with a stirrer, the air in the autoclave being displaced by nitrogen gas. The autoclave was closed and heated up to 250°C, with continuous stirring. After 30 minutes reaction at this temperature, the COD has fallen to 0.5 g/litre, the nitrate nitrogen concentration to 4.2 g/litre and the Kjeldahl nitrogen concentration to 15 g/litre. After cooling down to 32°C the gas phase contained 62% by volume of nitrogen gas, 35.3% of CO and CO ₂ , 1.5% of dinitrogen monoxide and less than 0.01% of nitrous fumes. The liquid phase contained 0.1 g/litre of nitrate nitrogen and 10.4 g/litre of Kjeldahl nitrogen.	70 75 80
I was lactam apora- onium action 158.0 1200 255°C gauge. forcing xygen atmos- actica	85 90 95	15 Air was displaced from the autoclave with nitrogen, the autoclave was closed, and heated to 300°C over a period of time of 3 hours. The temperature was maintained for 1 hour, after which the autoclave and its contents were cooled to 35°C over a period of time of 18 hours. The pressure in the autoclave was then 15 bars.	Comparative Experiment The procedure of Example X was repeated with a reaction mixture containing 25.2 g/litre of COD, 28.4 g/litre of nitrate nitrogen and 38.7 g/litre of Kjeldahl nitrogen, the reaction temperature being 123—147°C and reaction time 125 minutes. After cooling down to 30°C the liquid phase contained 25.0 g/litre of COD, 25.6 g/litre of nitrate nitrogen and 38.9 g/litre of Kjeldahl nitrogen. No degradation of impurities had taken place.	85 90 95
COD value, minutes in the	100	20 During the reaction the chemical oxygen demand of the reaction mixture decreases to 16% of the initial value. 51% of the converted nitric acid was converted in to molecular nitrogen 4,6% into dinitrogen monoxide and to 3% into nitrous fumes mainly nitrogen monoxide.	EXAMPLE XI The procedure of Example X was repeated with a reaction mixture containing 28.0 g/litre of COD, 26.8 g/litre of nitrate nitrogen and 37.8 g/litre of Kjeldahl nitrogen, the reaction temperature being 185°C and reaction time 80 minutes. After cooling to 32°C the liquid phase contained 18.8 g/litre of COD, 20.4 g/litre of nitrate nitrogen and 33.1 g/litre of Kjeldahl nitrogen. The gas phase contained 70% by volume of nitrogen gas, 29.2% of CO and CO ₂ , 0.66% of N ₂ O and 0.02% of nitrous fumes.	100 105 110
mples COD n con- n did e, but l. The	105	25 Slow heating of the reaction is to be preferred to fast heating, the corrosiveness of the mixture during the reaction being thereby reduced.	WHAT WE CLAIM IS:— 1. A process for the treatment of a waste water whereby carbonaceous contaminants contained in the waste water are converted to gaseous reaction products comprising oxidizing the said contaminants in the waste water with an oxidation agent which is nitric acid and/or a nitrate at a temperature between 150°C and the critical temperature of the water containing the contaminants.	105 110 115
len to minutes l.	110	30 The procedure of Example VII was repeated using an 85% excess of nitric acid based on the COD content of the liquid. During the reaction, the COD of the reaction mixture decreased to below 0.1% of the original value. 36% of the converted nitric acid was converted into molecular nitrogen, 29% into dinitrogen monoxide and 35% into nitrous fumes mainly nitrogen monoxide. The use of such a large excess of nitric acid while resulting in the generation of a considerable amount of nitrous fumes, nevertheless effects complete breakdown of the organic impurities.	2. A process according to Claim 1, in which the process is carried out at a temperature above 220°C.	110 115 120
ded to ivated d the ed at The action initial r was r had COD g/litre ibuted	115 120 125	35 EXAMPLE VIII The procedure of Example VII was repeated using an 85% excess of nitric acid based on the COD content of the liquid. During the reaction, the COD of the reaction mixture decreased to below 0.1% of the original value. 36% of the converted nitric acid was converted into molecular nitrogen, 29% into dinitrogen monoxide and 35% into nitrous fumes mainly nitrogen monoxide. The use of such a large excess of nitric acid while resulting in the generation of a considerable amount of nitrous fumes, nevertheless effects complete breakdown of the organic impurities.	3. A process according to Claim 2, in which	115 120 125
		40 EXAMPLE IX The procedure of Example VII was followed using a 125% excess of nitric acid, the reaction mixture further containing 1120 g/litre of ammonium sulfate, but no sodium sulfate. During the reaction, the COD of the reaction mixture decreased to 10% of the initial value. 96% of the converted nitric acid was converted into molecular nitrogen and to 4% into dinitrogen monoxide. Nitrous fumes were not formed in detectable quantities. The content of ammonium nitrogen decreased to 63% of the initial value.		

the process is carried out at a temperature between 250°C and 310°C.

4. A process according to any of Claims 1 to 3, in which the oxidation agent is used in an amount less than 50% excess based on the amount of carbonaceous contaminants in the water waste.

5. A process according to Claim 4, in which the oxidation agent used is from 10% to 25% excess.

6. A process according to any of Claims 1 to 5, in which ammonium nitrate is used as the oxidation agent.

7. A process according to any of Claims 1 to 6, in which the water waste contains nitrogen compounds in addition to the carbonaceous contaminants.

8. A process according to Claim 7, in which the water waste contains an ammonium salt, the said water waste being derived from a chemical process in which an inorganic acid is converted into an ammonium salt con-

taminated with carbonaceous substances; in which nitric acid is employed as oxidation agent.

9. A process according to Claim 8, in which water waste is derived from the preparation of an unsaturated nitrite from a gas containing an alkene, ammonia and molecular oxygen.

10. A process for the treatment of a water waste according to Claim 1, substantially as hereinbefore described.

11. A process for the treatment of a water waste substantially as hereinbefore described in any of the Examples.

12. Water wastes purified by a process according to any of Claims 1 to 11.

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